# HYDROGEN ATOM - COMPLETE WAVE FUNCTION

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 4.43.

If we combine all the results from the solution of the angular and radial equations for the hydrogen atom, we get a formula for the spatial wave function, which is given in Griffiths's book as eqn 4.89:

$$\psi_{nlm}=\sqrt{\left(\frac{2}{na}\right)^{3}\frac{(n-l-1)!}{2n\left[(n+l)!\right]^{3}}}e^{-r/na}\left(\frac{2r}{na}\right)^{l}L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_{l}^{m}(\theta,\phi) \quad (1)$$

where $L$ is an associated Laguerre polynomial and $Y$ is a spherical harmonic.

The spherical harmonics can be calculated from a standard formula, as can the associated Laguerre polynomials. The forms of these functions vary according to the normalization. My version is

$$L_{p}^{q}(x)=c_{0}\sum_{j=0}^{p}\frac{(-1)^{j}(p+q)!}{(p-j)!(q+j)!j!}x^{j} \quad (2)$$

The version in Griffiths sets $c_0=(p+q)!$ (so it is that version that is used in the above formula for $\psi_{nlm}$) while some other sources use $c_0=1$.

For the spherical harmonics, the formulas are

$$Y_{l}^{m}(\theta,\phi)=\left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}e^{im\phi}P_{l}^{m}(\cos\theta) \quad (3)$$

with the $P_l^m$ being the associated Legendre function:

$$P_{l}^{m}(x)=(1-x^{2})^{m/2}\sum_{k=0}^{[(l-m)/2]}\frac{(2l-2k)!}{2^{l}(l-k)!k!(l-2k-m)!}(-1)^{k}x^{l-m-2k} \quad (4)$$

As an example of using this formula, we'll construct $\psi_{321}$. We get $L_0^5(x)=120$ and we worked out $Y_2^1$ in the previous post as

$$Y_{2}^{1}(\theta,\phi)=-\sqrt{\frac{15}{8\pi}}e^{i\phi}\sin\theta\cos\theta \quad (5)$$

Plugging these into the overall formula gives

$$\psi_{321} = -\sqrt{\left(\frac{2}{3a}\right)^3 \frac{1}{6\times 120^3}} e^{-r/3a}\left(\frac{2r}{3a}\right)^2 (120)\left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta e^{i\phi} \tag{6}$$

$$= -\frac{1}{81\sqrt{\pi a^7}} r^2 e^{-r/3a}\sin\theta\cos\theta e^{i\phi} \tag{7}$$

To check the normalization, we do the integral:

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi_{321}|^2 r^2 \sin\theta dr d\theta d\phi = \frac{1}{81^2\pi a^7}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^6 e^{-2r/3a}\sin^3\theta\cos^2\theta dr d\theta d\phi \tag{8}$$

$$= 1 \tag{9}$$

using Maple for the integral.

The expectation value of $r^s$ is (using Maple)

$$\langle r^s\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi_{321}|^2 r^{2+s}\sin\theta dr d\theta d\phi \tag{10}$$

$$= \frac{1}{81^2\pi a^7}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^{6+s} e^{-2r/3a}\sin^3\theta\cos^2\theta dr d\theta d\phi \tag{11}$$

$$= \frac{1}{720}\left(\frac{3a}{2}\right)^s \Gamma(7+s) \tag{12}$$

The gamma function is infinite at all non-positive integral arguments, so this value is finite for $s > -7$ and all non-integer values less than $-7$. The smallest integer value for which this is finite is $s = -6$. Note in particular that if $s = 0$, the formula reduces to $\langle r^0\rangle = 1$ as it should.

The expectation value of $r$ itself is

$$\langle r\rangle = \frac{21a}{2} \tag{13}$$

This is quite a bit bigger than the value for the ground state, which is $\langle r\rangle = 3a/2$.

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